

AD-A041 976

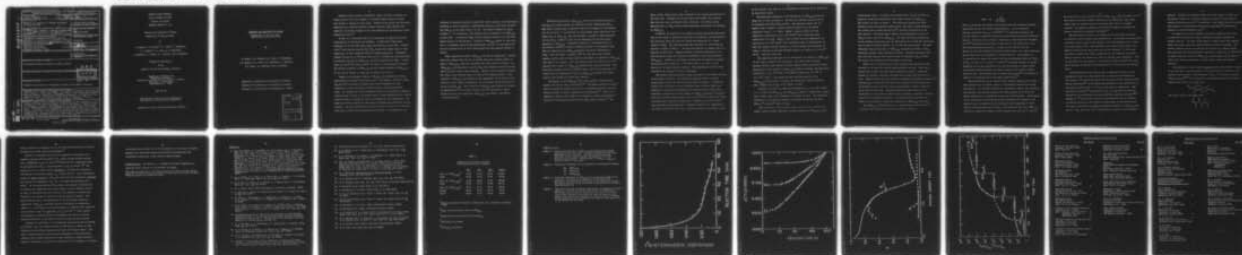
PENNSYLVANIA UNIV PHILADELPHIA LAB FOR RESEARCH ON --ETC F/G 7/2  
SYNTHESIS AND PROPERTIES OF HALOGEN DERIVATIVES OF (SN)X AND (C--ETC(U)  
JUL 77 M AKHTAR, C K CHIANG, M J COHEN N00014-75-C-0962

UNCLASSIFIED

LRSM-TR-77-2

NL

| OF |  
AD  
A041 976



END

DATE  
FILMED  
8-77

## REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS  
BEFORE COMPLETING FORM

1. REPORT NUMBER Technical Report No. 77-2	2. GOVT ACCESSION NO. (14) LRSM-TR-77-21	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Synthesis and Properties of Halogen Derivatives of (SN) <sub>x</sub> and (CH) <sub>x</sub>	5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report	
6. PERFORMING ORG. REPORT NUMBER		7. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0962
8. AUTHOR(s) M. Akhtar, C. K. Chiang, M. J. Cohen, J. Kleppinger, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, J. Milliken, M. J. Moran, D. L. Peebles, & H. Shirakawa		9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-356-062
10. PERFORMING ORGANIZATION NAME AND ADDRESS Departments of Chemistry and Physics and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pa. 19104		11. REPORT DATE July 1977
12. CONTROLLING OFFICE NAME AND ADDRESS Department of The Navy Office of Naval Research Arlington, Virginia 22217		13. NUMBER OF PAGES Twenty-one
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Distribution unlimited; approved for public release		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) DDC RECEIVED JUL 22 1977 A		
18. SUPPLEMENTARY NOTES Prepared for publication in the Annals of the New York Academy of Sciences		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) polymeric sulfur nitride, polythiazyl, (SN) <sub>x</sub> , optical properties, electron properties, (SNBr <sub>0.4</sub> ) <sub>x</sub> , (SNBr <sub>0.55</sub> ) <sub>x</sub> , (SNBr <sub>0.05</sub> ) <sub>x</sub> , density, X-ray, electrical resistance, metallic behavior, conductivity, bromination, plasma edge, polyacetylene, (CH) <sub>x</sub> , conjugated polyene, semiconductors, trans-isomer, (CHBr <sub>0.05</sub> ) <sub>x</sub> , (CHBr <sub>0.23</sub> ) <sub>x</sub> , (CHI <sub>0.22</sub> ) <sub>x</sub> , (CHI <sub>0.05</sub> ) <sub>x</sub> , activation energy, polarized reflectance		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Metallic polymeric sulfur nitride may be halogenated at room temperature to give a series of highly conducting polymers which are also metals. Compositions such as (SNBr <sub>0.23</sub> ) <sub>x</sub> , (SNBr <sub>0.4</sub> ) <sub>x</sub> , and (SNBr <sub>0.55</sub> ) <sub>x</sub> may be obtained under varying conditions. The conductivity of (SNBr <sub>0.4</sub> ) <sub>x</sub> is ten times greater than that of (SN) <sub>x</sub> itself. Crystalline silvery films of the flexible semiconducting polymer, trans "polyacetylene," take up halogens with enhanced optical and electrical properties. (CHBr <sub>0.03</sub> ) <sub>x</sub> and (CHI <sub>0.22</sub> ) <sub>x</sub> have four and seven orders of magnitude greater room temperature conductivities respectively, than trans-(CH) <sub>x</sub> .		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE  
S/N 0102-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

279 025

ADA041976

DDC FILE COPY

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0962

Task No. NR 356-602

TECHNICAL REPORT NO. 77-2

Synthesis and Properties of Halogen

Derivatives of  $(\text{SN})_x$  and  $(\text{CH})_x$

by

M. Akhtar, C. K. Chiang,<sup>†</sup> M. J. Cohen,<sup>†</sup> J. Kleppinger,  
A. J. Heeger,<sup>†</sup> E. J. Louis, A. G. MacDiarmid,  
J. Milliken, M. J. Moran, D. L. Peebles,<sup>†</sup> and H. Shirakawa

Prepared for Publication

in the

Annals of the New York Academy of Sciences

Department of Chemistry and  
<sup>†</sup>Department of Physics,  
Laboratory for Research on the Structure of Matter,  
University of Pennsylvania,  
Philadelphia, Pa. 19104

July 18, 1977

Reproduction in whole or part is permitted for  
any purpose of the United States Government

Approved for public release; distribution unlimited.

SYNTHESIS AND PROPERTIES OF HALOGEN

DERIVATIVES OF (SN)<sub>x</sub> AND (CH)<sub>x</sub>

by

M. Akhtar, C.K. Chiang,\* M.J. Cohen,\* J. Kleppinger,  
A.J. Heeger,\* E.J. Louis, A.G. MacDiarmid, J. Milliken,  
M.J. Moran, D.L. Peebles,\* and H. Shirakawa

Department of Chemistry and \*Department of Physics,  
Laboratory for Research on the Structure of Matter,  
University of Pennsylvania, Philadelphia, PA 19104

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DDC	Bull. Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION AVAILABILITY CODES	
Dist.	AVAIL. and SPECIAL
A	



Polymeric sulfur nitride, polythiazyl,  $(\text{SN})_x$ , has been of interest in recent years as the first example of a covalent polymer which is a metal even though it contains no metal atoms. Studies of the optical and electronic properties have indicated metallic behavior along the  $(\text{SN})_x$  chains<sup>1</sup> with sufficient interchain coupling to give the properties of an anisotropic three dimensional metal.<sup>2,3</sup>

As part of a continuing study of the properties of  $(\text{SN})_x$  we have been investigating its reactions with halogens. In 1969 Patton<sup>4</sup> made brief reference to the fact that  $(\text{SN})_x$  reacts with chlorine to give  $\text{NSCl}$ . Bernard et al.<sup>5</sup> have reported recently that  $(\text{SN})_x$  reacts with bromine vapor at room temperature to give a gray-blue solid of unknown composition. Independent studies carried out by us<sup>6</sup> and by Street et al.<sup>7</sup> involved the characterization of crystals and films of  $(\text{SNBr}_{0.4})_x$ , the first derivative of  $(\text{SN})_x$ . In this paper we report<sup>8</sup> the initial results of studies of the electrical transport and optical properties of  $(\text{SNBr}_{0.4})_x$  and the related derivative  $(\text{SNBr}_{0.25})_x$ . We also report studies on  $(\text{CH})_x$  and its halogen derivatives.

Samples of polythiazyl bromides,  $(\text{SNBr}_y)_x$ , were prepared by reacting analytically pure  $(\text{SN})_x$ <sup>9</sup> with bromine vapor. For example, crystals of  $(\text{SN})_x$  (ca 1-10 mm<sup>3</sup>) in 60 torr of bromine vapor react immediately at room temperature to give shiny black crystals having a lustrous blue-purple tinge. The composition of the brominated material was determined by exposing a known weight of  $(\text{SN})_x$  to the bromine vapor. Excess bromine was then removed from the product by pumping it for 5 to 15 minutes at room temperature. The weight of bromine absorbed was determined by weighing the polythiazyl bromide produced. The time required for the maximum amount of bromine to be absorbed under these conditions was approximately 40 minutes. The composition was

confirmed by elemental analysis; compositions varied slightly, but significantly, according to minor variations in experimental procedure, with values obtained for  $(\text{SNBr}_y)_x$  in the range  $0.38 \leq y \leq 0.42$ . Two typical analyses are given in Table 1. For convenience, this material will be referred to as  $(\text{SNBr}_{0.4})_x$  in this paper. No unreacted  $(\text{SN})_x$  could be detected visually or in the x-ray powder patterns of the material. Crystals of  $(\text{SNBr}_{0.4})_x$  appear to react with air to a negligible extent during approximately one hour at room temperature but are tarnished after 10 hours during which time some ammonium bromide is formed.

Other compositions besides  $(\text{SNBr}_{0.4})_x$  can also be synthesized. Crystals which were weighed under 60 torr of bromine vapor had a bromine content as high as  $(\text{SNBr}_{0.55})_x$ . Material containing only small amounts of bromine, e.g.  $(\text{SNBr}_{0.05})_x$ , was prepared by reacting  $(\text{SN})_x$  with bromine for shorter periods and/or at lower bromine vapor pressures. However, some of these compositions may contain some unreacted  $(\text{SN})_x$  and will not be discussed further. When crystals of  $(\text{SNBr}_{0.4})_x$  were pumped at room temperature for 45 hours or more, there was little change in appearance, but the bromine content decreased to as low as  $(\text{SNBr}_{0.33})_x$ . When crystals of  $(\text{SNBr}_{0.4})_x$  were heated with pumping at approximately  $86^\circ\text{C}$  for about 30 hours they were converted to copper-colored crystals with composition  $(\text{SNBr}_{0.25})_x$  (see Table 1) and density  $2.54 \pm 0.06 \text{ g/cm}^3$ .

Polycrystalline metallic  $(\text{SNBr}_{0.25})_x$  can also be synthesized directly from  $\text{S}_4\text{N}_4$  and bromine without the necessity of first synthesizing  $(\text{SN})_x$ . When finely powdered  $\text{S}_4\text{N}_4$  is exposed to 180 torr of bromine at room temperature for 16 hours, it is converted to a black powder whose composition from weight gain is  $(\text{SNBr}_{1.5})_x$ . When this material is pumped at room temperature for four hours, bromine is lost and the composition of the black powder remaining is  $(\text{SNBr}_{0.4})_x$ . Preliminary studies on a compressed pellet of this material showed it to have a conductivity which is considerably lower than the conductivity of  $(\text{SNBr}_{0.4})_x$  formed by the direct bromination of  $(\text{SN})_x$ . When the powder is heated at  $80^\circ\text{C}$  for four hours with constant pumping, an 82% yield of a dark copper-colored powder of composition  $(\text{SNBr}_{0.25})_x$  (see Table I) is obtained. Its x-ray powder pattern is identical with that obtained from a sample of  $(\text{SNBr}_{0.25})_x$  prepared from  $(\text{SN})_x$  and bromine. This observation together with data presented below, lead to the surprising conclusion that the bromination of  $\text{S}_4\text{N}_4$  to  $(\text{SNBr}_{0.25})_x$  involves the polymerization of the cradle-like cyclic  $\text{S}_4\text{N}_4$  molecule.

The density of the  $(\text{SNBr}_{0.4})_x$  ( $2.67 \pm 0.04 \text{ g/cm}^3$ ) is significantly greater than that of  $(\text{SN})_x$  ( $2.30 \text{ g/cm}^3$ ).<sup>6,7</sup> The volume increase calculated from the formula and density data is 46%, in reasonable agreement with the observed changes in crystal dimensions upon bromination.<sup>6,7</sup> There is no significant change in the length of the crystal in the b crystallographic direction (the direction parallel to the  $(\text{SN})_x$  polymer chains).<sup>6,7</sup> The



entire volume change results from a swelling of the crystal perpendicular to the chain axis. Although the crystals appear well-formed, X-ray studies show they have very considerable defect structure. The fibrous nature characteristic of  $(\text{SN})_x$  crystals when mechanically pulled apart is preserved in  $(\text{SNBr}_{0.4})_x$ .

To monitor the kinetics of the chemical reaction and provide definitive data on the change in electrical resistance on bromination, we have measured the resistance along the chain axis during the bromination of a single crystal of  $(\text{SN})_x$ . The resulting normalized resistance vs. time during the reaction is shown in Figure 1. The data were obtained in bromine vapor at a pressure of 20-25 torr. Chemical analysis of crystals brominated in the same experiment showed the reaction had proceeded to give the composition  $(\text{SNBr}_{0.40})_x$ . Contacts to the sample were made with the graphite suspension Electrodag (Acheson Colloid Co., Port Huron, Mich.) in order to avoid reaction of the usual metallic contacts. The measurements were made using four-probe low frequency (37 Hz) ac techniques.

The initial reaction proceeds rapidly and results in an obvious decrease in the sample resistance. The resistance eventually falls to a value approximately 0.05 of the initial value as shown in Figure 1. Taking into account the ~46% increase in cross-sectional area, we find a final room temperature conductivity approximately 13 times the initial  $(\text{SN})_x$  value. Independent measurements on five samples of  $(\text{SNBr}_{0.4})_x$  mounted for measurement after reaction yielded values from  $1.4 \times 10^4$  to  $9.1 \times 10^4 (\Omega\text{-cm})^{-1}$  with an average room temperature conductivity,  $\sigma_{||}(300 \text{ K}) = 3.8 \times 10^4 (\Omega\text{-cm})^{-1}$ . Room temperature measurements of  $\sigma_{\perp}$  yielded  $8 (\Omega\text{-cm})^{-1}$ , i.e. comparable to the values obtained for pure  $(\text{SN})_x$ . However, because of the fibrous nature



of the crystals, the value for  $\sigma_1$  is probably not intrinsic but is determined by inter-fibre contact.

The temperature dependence of the resistivity of  $(\text{SNBr}_{0.4})_x$  along the chain axis is shown in Figure 2. The data were obtained using four-probe dc techniques with Electrodag contacts. The normalized results for two samples shown in Figure 2 indicate metallic behavior over the entire temperature range  $4 < T < 300$  K. Sample 1 (closed circles) had room temperature conductivity of  $9.1 \times 10^4 (\Omega\text{-cm})^{-1}$  and a resistance ratio  $\rho(300 \text{ K})/\rho(4.2 \text{ K}) \approx 90$ . Sample 2 (open circles) had room temperature conductivity of  $1.4 \times 10^4 (\Omega\text{-cm})^{-1}$  and a resistance ratio of approximately 12. Note that sample 2 becomes residual at  $T \leq 10$  K whereas the resistivity of sample 1 continues to decrease becoming residual at a value  $\rho_0 \approx 1.2 \times 10^{-7} (\Omega\text{-cm})$  only well below 10 K.

The temperature dependence of the resistivity of a crystal of  $(\text{SNBr}_{0.25})_x$  is also shown on Figure 2 for comparison. The results again indicate metallic behavior with typically somewhat larger residual resistivity values. Measurements on six samples of  $(\text{SNBr}_{0.25})_x$  yielded an average room temperature conductivity of  $2 \times 10^4 (\Omega\text{-cm})^{-1}$  with values ranging from  $0.9 \times 10^4$  to  $5.9 \times 10^4 (\Omega\text{-cm})^{-1}$ . Dark copper-colored compressed pellets of the  $(\text{SNBr}_{0.25})_x$  formed directly from  $\text{S}_4\text{N}_4$  and bromine were highly conducting, with a conductivity of ca  $1 \times 10^2 (\Omega\text{-cm})^{-1}$  at  $25^\circ\text{C}$ .

Attempts to analyze the temperature dependence as  $\rho = \rho_0 + AT^n$  yielded  $1 < n < 2$  for both  $(\text{SNBr}_{0.4})_x$  and  $(\text{SNBr}_{0.25})_x$ . However, log-log plots suggest that a single power law is inadequate to describe the data. The temperature dependence of the brominated material is somewhat weaker than the well-defined  $T^2$  behavior<sup>10</sup> found in  $(\text{SN})_x$ .

Upon bromination,  $(\text{SN})_x$  crystals change color from the characteristic highly reflecting golden appearance to black crystals of  $(\text{SNBr}_{0.4})_x$  having

a blue-purple tinge. To examine this quantitatively, we have carried out polarized reflectance measurements from single crystals of  $(\text{SNBr}_{0.4})_x$ . The results are shown in Figure 3. The reflectance spectrum for light polarized along the principal conducting axis ( $R_{\parallel}$ ) shows a broad minimum in the visible with a plasma edge  $\hbar\omega_p/(\epsilon_{\infty}^{1/2})$  and high reflectivity in the near infrared. The plasma edge is shifted from approximately 2.55 eV in  $(\text{SN})_x$  to about 1.65 eV for  $(\text{SNBr}_{0.4})_x$ . For light polarized perpendicular to the principal conducting axis, the reflectance ( $R_{\perp}$ ) is flat and featureless with no sign of metallic behavior ( $R_{\perp} \sim 3\%$  over the entire range). The long wavelength optical anisotropy of  $(\text{SNBr}_{0.4})_x$  is greater than that of  $(\text{SN})_x$  indicating somewhat weaker interchain coupling. Polarized reflectance data have also been obtained from oriented films of brominated  $(\text{SN})_x$  on Mylar. The results are consistent with the single crystal data.

Below 1 eV,  $R_{\parallel}$  decreases rather than asymptotically approaching 100% as would be the case for a simple Drude dielectric function. Since the dc conductivity is high, the most likely explanation involves a relatively strong low frequency interband transition with corresponding structure in  $\epsilon(\omega)$ . Similar effects have been observed in graphite intercalation compounds.<sup>11</sup> Alternatively, the decrease may result from structure in  $\epsilon(\omega)$  arising from a pseudogap related to the more nearly one-dimensional behavior suggested by the optical anisotropy. Detailed reflectance measurements into the intermediate and far infrared regions will be required to develop a complete picture of the dielectric function. Our initial studies presented here focus on the oscillator strength and comparison of  $(\text{SNBr}_{0.4})_x$  with  $(\text{SN})_x$ .

The  $(\text{SNBr}_{0.4})_x$  reflectance data,  $R_{\parallel}$ , were analyzed in the vicinity of the plasma edge assuming a simple Drude dielectric function

$$\epsilon(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega/\tau}$$

where  $\epsilon_{\infty}$  represents the combined contributions from high frequency interband transitions and the core atomic polarizabilities,  $\tau$  is the conduction electron scattering time,  $\omega_p = (4\pi Ne^2/m^*)^{1/2}$  is the plasma frequency, and  $N$  is the number of conduction electrons per unit volume with optical effective mass  $m^*$ . The solid curve on Figure 3 represents a least-square fit (weighted by  $R^{-1/2}$ ) arbitrarily restricting the input data to the range above 1.1 eV. The resulting parameters are  $\hbar\omega_p = 4.8$  eV,  $\epsilon_{\infty} = 8.7$  and  $\hbar/\tau \approx 0.4$  eV. Because of the clear deviation from Drude behavior below 1 eV, these parameters can be taken only as an indication of overall behavior. Nevertheless, it is instructive to compare the results with the corresponding values for  $(\text{SN})_x$ , of  $\hbar\omega_p = 5.1$  eV,  $\epsilon_{\infty} = 4.2$  and  $\hbar/\tau = 0.55$  eV.<sup>12</sup> The small decrease in plasma frequency is more than accounted for by the  $\sim 46\%$  increase in sample volume on bromination indicating that any charge transfer to the bromine acceptor states is weak. The downward shift in plasma edge  $\hbar\omega_p/(\epsilon_{\infty}^{1/2})$  on bromination appears to be primarily due to the larger value for  $\epsilon_{\infty}$ .<sup>13</sup>

Visual observation of the crystals after reaction suggests that bromination decreases the crystalline quality. X-ray studies confirm these latter observations. The brominated material is crystalline; however, the relatively well-defined x-ray patterns obtained from  $(\text{SN})_x$  crystals become broad and diffuse indicative of a significant decrease in crystal quality. Nevertheless, the dc conductivity studies described above demonstrate an increase in the absolute value of conductivity with resistance ratios comparable to those found in relatively high quality  $(\text{SN})_x$ . The reflectance data from  $(\text{SNBr}_{0.4})_x$  indicate no significant change in  $(N/m^*)$  compared with  $(\text{SN})_x$  and a value for



$\hbar/\tau$  comparable to that typically found for  $(\text{SN})_x$  ( $\sigma_{\text{opt}} = \frac{1}{4\pi} \omega_p^2 \tau \approx 7000 (\Omega\text{-cm})^{-1}$ ). These results therefore provide evidence that the fundamental  $(\text{SN})_x$  chains remain intact as bromine enters the structure with little or no charge transfer. The combined transport and optical data suggest an analogy with bromine intercalation compounds of graphite.<sup>14</sup>

The observation of little or no charge transfer from  $(\text{SN})_x$  to bromine is consistent with the known electronegativities. The Pauling electronegativity of bromine (2.8) is equal to the average of the electronegativities of sulfur (2.5) and nitrogen (3.0). The possibility that charge transfer might occur from the bromine to the  $(\text{SN})_x$  chain may even be considered. In this case, the charge transfer would tend to compensate for the reduction in electron density caused by the increase in volume of the  $(\text{SN})_x$  upon bromination. This is consistent with the suggestion from Schottky barrier studies<sup>15</sup> that  $(\text{SN})_x$  may be assigned an effective electronegativity of 2.9 or more on the Pauling scale.

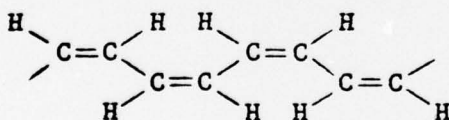
The observation of more than an order of magnitude increase in room temperature conductivity upon bromination is particularly interesting in the context of the optical properties and the poorer overall crystal quality. Earlier measurements<sup>10</sup> of the temperature dependence of the conductivity of pure  $(\text{SN})_x$  indicated that  $\rho \propto T^2$  over a wide range of temperatures. Band structure calculations<sup>16</sup> characterized  $(\text{SN})_x$  as a semi-metal in which the resistivity may be dominated by electron-electron scattering processes<sup>10,17</sup> leading to a  $T^2$  term in the resistivity with magnitude which is sensitive to detailed features of the electron and hole pieces of the Fermi surface. The higher conductivity and weaker temperature dependence of  $(\text{SNBr}_{0.4})_x$  compared to  $(\text{SN})_x$  imply that the  $T^2$  contribution is smaller in the brominated



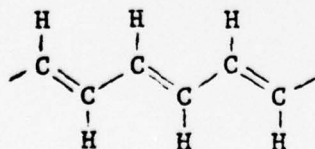
compound. Evidently the combined effects of a small change in  $(N/m^*)$  and the implied decrease in interchain coupling as inferred from the optical studies partially quench the  $T^2$  contribution. Such effects have been predicted from analysis of electron-hole scattering in semi-metals<sup>18</sup> and have been observed in non-stoichiometric  $TiS_2$ .<sup>19</sup>

In summary, our initial transport and optical studies of this class of brominated derivatives of  $(SN)_x$ , polythiazyl bromides, demonstrate metallic behavior. The  $(SN)_x$  chains appear to remain intact with somewhat weaker interchain coupling as inferred from the optical anisotropy. The bromine evidently enters the structure with little or no charge transfer. The relatively high room temperature conductivity,  $\sigma(300\text{ K}) \sim 4 \times 10^4 (\Omega\text{-cm})^{-1}$ , in highly defected crystals of  $(SNBr_{0.4})_x$  is encouraging from the point of view of the eventual possibility of useful highly conducting synthetic polymers.

In attempting to find a covalent organic polymer which would be a metal or at least have a high conductivity, we have focused our attention on the simplest organic polymer, "polyacetylene",  $(CH)_x$ . In a series of studies, Shirakawa *et al.*<sup>20-24</sup> have succeeded in synthesizing high quality flexible copper-colored films of the cis isomer



and silvery films of the trans isomer



of this conjugated polyene from acetylene in the presence of a Ziegler catalyst, and they have developed techniques for controlling the cis and trans content.<sup>22,23</sup> X-ray diffraction and scanning electron micrograph studies show that films of any cis and trans composition are crystalline and consist of matted fibrils.<sup>22</sup> These materials are semiconductors;<sup>24</sup> the trans isomer, which is the thermodynamically stable form at room temperature, has a higher conductivity ( $\sigma_{273\text{ K}} = 4.4 \times 10^{-5} (\Omega\text{-cm})^{-1}$ ) than the cis isomer ( $\sigma_{273\text{ K}} = 1.7 \times 10^{-9} (\Omega\text{-cm})^{-1}$ ).<sup>24</sup>

Shirakawa and Ikeda<sup>25</sup> have noted that when  $(\text{CH})_x$  films are exposed to bromine or chlorine vapor at room temperature for a few minutes, a dramatic decrease in infrared transmission ( $4,000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ ) occurs without any visible change in appearance of the films. Complete halogenation to yield, e.g.  $(\text{CHBr})_x$ , results again in high infrared transmission with concomitant production of a white film. The initial reduction in infrared transmission suggests that the halogen-doped material might have unusual electronic properties. The results of studies involving the halogenation of films of trans-( $\text{CH}$ )<sub>x</sub> are summarized below.

The conductivity of the  $(\text{CH})_x$  films was measured by four-probe dc techniques at room temperature in a glass vessel to which was attached a bulb containing the halogen. This bulb was held at various temperatures to produce known halogen vapor pressures. When  $(\text{CH})_x$  is exposed to 1 torr of bromine vapor at room temperature for 10 min. the conductivity rapidly increases by approximately four orders of magnitude to give silvery films of  $(\text{CHBr}_{0.05})_x$  having a conductivity of  $0.5 (\Omega\text{-cm})^{-1}$  at room temperature. Longer bromination gives silvery-black films having the composition  $(\text{CHBr}_{0.23})_x$  and a slightly smaller conductivity ( $\sigma_{298\text{ K}} = 0.4 (\Omega\text{-cm})^{-1}$ ). The films are stable both in

vacuum and when exposed to air for at least several hours at room temperature. Qualitatively similar results are obtained with chlorine, but the increase in conductivity is smaller (about three orders of magnitude).

When iodine vapor reacts with  $(CH)_x$  at room temperature, the infrared transmission decreases in a manner similar to that described above for bromine. However, the increase in conductivity is even more remarkable, over seven orders of magnitude, as shown in Figure 4. The maximum conductivity ( $\sigma_{298\text{ K}} = 38 (\Omega\text{-cm})^{-1}$ ) was observed on a silvery-black film of composition  $(CHI_{0.22})_x^*$ . The appearance of the  $(CH)_x$  film remained essentially unchanged until the approximate composition  $(CHI_{0.05})_x$  was reached, after which it began to darken. The stability of the iodinated films is similar to that of the brominated material. Separate measurements of three samples of  $(CHI_{0.22})_x$  gave an average conductivity of  $30 (\Omega\text{-cm})^{-1}$ . This material has the largest room temperature conductivity observed for any covalent organic polymer.

We believe that charge-transfer complexes are formed between  $(CH)_x$  and halogens when they are permitted to react under certain conditions, as has been observed previously with iodine and polyphenylene.<sup>26</sup> However, in the case of  $(CH)_x$  the absolute conductivities obtained are four to five orders of magnitude greater.

The highly conducting polyacetylene bromides and iodides may be charge-transfer pi complexes of the type believed to be formed during the halogenation of olefins. Stable colored compounds which may be charge-transfer

---

\* Analytical data (Galbraith Laboratories, Inc., Knoxville, Tenn. 37921): Calcd. for  $(CHI_{0.22})_x$ , C, 29.34; H, 2.46; I, 68.20. Found: C, 29.14; H, 2.62; I, 68.26%.  $\times$  (Total = 100.02%).



and/or carbonium ion complexes of this type have been obtained by the action of bromine on certain substituted ethylenes.<sup>27</sup>

We note for comparison that the room temperature conductivity of a compacted, polycrystalline pellet of the organic charge-transfer metallic salt, (TTF)<sup>+</sup>(TCNQ)<sup>-</sup> is ca.  $10 (\Omega\text{-cm})^{-1}$ ,<sup>28</sup> while that of a compressed pellet of polycrystalline (SN)<sub>x</sub> at room temperature is ca.  $20 (\Omega\text{-cm})^{-1}$ .<sup>29</sup> The conductivity of the latter material decreases on lowering the temperature and exhibits an activation energy,  $E_a$ , of about 0.02 eV. Later experimental results on single crystals of (SN)<sub>x</sub> have shown that the conductivity increases with decrease in temperature, ( $E_a = 0$ ), in a manner characteristic of a metal.<sup>1</sup> In the polycrystalline (SN)<sub>x</sub> sample, the increase in conductivity on lowering the temperature which occurs within a small, metallic crystal of (SN)<sub>x</sub> is apparently more than off-set by the decrease in conductivity involved in the passage of electrons from one crystal to another. Like polycrystalline (SN)<sub>x</sub>, the conductivity of the most highly conducting composition, (CHI<sub>0.22</sub>)<sub>x</sub>, decreases slowly on decreasing the temperature ( $300 \text{ K} > T > 4.2 \text{ K}$ ) with an activation energy,  $E_a \approx 0.016 \text{ eV}$  (for comparison the activation energy for trans-(CH)<sub>x</sub> is  $E_a \approx 0.3 \text{ eV}$ ).<sup>24</sup> These results are suggestive of metallic behavior; experiments are underway directed toward clarification of the origin of the very small activation energy.

Although the randomness of the halogenated polyacetylene may be playing an important role, the overall behavior is like that of a series of semiconductors with activation energies which vary with halogen content. However, a detailed study of the temperature dependence of the conductivity indicates that a simple semiconductor model involving a single activation energy is inadequate to describe the conductivity of the material. We believe



the polyacetylene halides may be the forerunners of a new class of organic polymers with electrical properties which may be systematically and controllably varied over a wide range by chemical doping.

Acknowledgement: We thank Dr. A. J. Epstein for helpful suggestions on achieving stable contacts in the presence of bromine.

This work was supported by the National Science Foundation by MRL program grant DMR 76-00678 and by grant CHE-73-04771-A03 and by the Office of Naval Research contract No. N00014-75-C-0962.

# References

1. See, for example, V. V. Walatka, Jr., M. M. Labes, and J. H. Perlstein, *Phys. Rev. Lett.* 31, 1139 (1973); C. Hsu and M. M. Labes, *J. Chem. Phys.* 61, 4640 (1974); C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito and A. J. Heeger, *J. Amer. Chem. Soc.* 97, 6358 (1975); R. L. Greene, P. M. Grant, and G. B. Street, *Phys. Rev. Lett.* 34, 89 (1975); R. L. Greene, G. B. Street, and L. J. Suter, *Phys. Rev. Lett.* 34, 577 (1975); M. J. Cohen, A. F. Garito, A. J. Heeger, A. G. MacDiarmid, C. M. Mikulski, M. S. Saran and J. Kleppinger, *J. Amer. Chem. Soc.* 98, 3844 (1976); R. H. Baughman, P. A. Apgar, R. R. Chance, A. G. MacDiarmid and A. F. Garito, *J. Chem. Phys.* 66, 401 (1977); H. P. Geserich and L. Pintschovius, in *Festkörperprobleme (Advances in Solid State Physics)*, Vol. XVI, p. 65, J. Treusch (ed.), Vieweg, Braunschweig (1976).
2. A. A. Bright, M. J. Cohen, A. F. Garito and A. J. Heeger, C. M. Mikulski and A. G. MacDiarmid, *Appl. Phys. Lett.* 26, 612 (1975).
3. C. H. Chen, J. Silcox, A. F. Garito, A. J. Heeger, and A. G. MacDiarmid, *Phys. Rev. Lett.* 36, 525 (1976).
4. R. L. Patton, Ph.D. Thesis, University of California, Berkeley, (1969).
5. C. Bernard, A. Herold, M. Lelaurain and G. Robert, *C. R. Acad. Sc. Paris*, C, 283, 625 (1976).
6. M. Akhtar, J. Kleppinger, A. G. MacDiarmid, J. Milliken, M. J. Moran, C. K. Chiang, M. J. Cohen, A. J. Heeger and D. L. Peebles, *Chem. Commun.*, in press.
7. G. B. Street, W. D. Gill, R. H. Geiss, R. L. Greene and J. J. Mayerle, *Chem. Commun.*, in press; W. D. Gill, W. Bludau, R. H. Geiss, P. M. Grant, R. L. Greene, J. J. Mayerle, and G. B. Street, *Phys. Rev. Lett.* 38, 1305 (1977).
8. A preliminary version of this study was presented as a post-deadline contributed paper at the American Physical Society Meeting, San Diego, California, March 23, 1977. Similar results were reported at the same time by G. B. Street, *et al.* (see Ref. 7).
9. C. M. Mikulski, A. G. MacDiarmid, A. F. Garito and A. J. Heeger, *Inorg. Chem.* 15, 2943 (1976).
10. C. K. Chiang, M. J. Cohen, A. F. Garito, A. J. Heeger, C. M. Mikulski and A. G. MacDiarmid, *Solid State Commun.* 18, 1451 (1976).
11. J. E. Fischer, T. E. Thompson, G. M. T. Foley, D. Guerard, M. Hoke and F. L. Lederman, *Phys. Rev. Lett.* 37, 769 (1976).
12. Marshall J. Cohen, Ph.D. Thesis, University of Pennsylvania (1975). Similar results have been obtained for  $(\text{SN})_x$  by others; see P. M. Grant, R. L. Greene, and G. B. Street, *Phys. Rev. Lett.* 35, 1743 (1975).

13. This point has been emphasized by W. D. Gill, private communication.
14. D. A. Platts, D. D. L. Chung and M. S. Dresselhaus, Phys. Rev. B 15, 1087 (1977).
15. R. A. Scranton, J. B. Mooney, J. O. McCaldin, T. C. McGill and C. A. Mead, Appl. Phys. Lett. 29, 46 (1976).
16. See, for example, the following: W. E. Rudge and P. M. Grant, Phys. Rev. Lett. 35, 1799 (1975); A. A. Bright and P. Soven, Sol. State Commun. 18, 317 (1976); M. Schlichter, J. R. Chelikowski and M. L. Cohen, Phys. Rev. Lett. 35, 869 (1975); W. I. Freisen, A. J. Berlinsky, B. Bergersen, L. Weiler, and T. M. Rice, J. Phys. C8, 3549 (1975).
17. A. A. Abrikosov, Introduction to the Theory of Metals, p. 67-73 (Academic Press, New York (1972)).
18. C. A. Kukkonen and P. F. Maldague, Phys. Rev. Lett. 37, 782 (1976).
19. A. H. Thompson, Phys. Rev. Lett. 35, 1786 (1975); and private communication.
20. H. Shirakawa and S. Ikeda, Polym. J. 2, 231 (1971).
21. H. Shirakawa, T. Ito and S. Ikeda, Polym. J. 4, 460 (1973).
22. T. Ito, H. Shirakawa and S. Ikeda, J. Polym. Sci. Polym. Chem. Ed. 12, 11 (1974).
23. T. Ito, H. Shirakawa and S. Ikeda, J. Polym. Sci. Polym. Chem. Ed. 13, 1943 (1975).
24. H. Shirakawa, T. Ito and S. Ikeda, (unpublished results) (1976).
25. H. Shirakawa and S. Ikeda, (unpublished results) (1976).
26. S. B. Mainthia, P. L. Kronick, H.U.E.F. Chapman and M. M. Labes, Polym. Prepr. Amer. Chem. Soc., Div. Polym. Chem. 4, No. 1, April (1963).
27. R. E. Buckles and N. A. Meinhardt, J. Amer. Chem. Soc. 74, 1171 (1952); R. E. Buckles and W. D. Womer, J. Amer. Chem. Soc. 80, 5058 (1958).
28. L. B. Coleman, Ph.D. Thesis, University of Pennsylvania (1975).
29. M. M. Labes, Pure Appl. Chem. 12, 275 (1966).

TABLE 1

Representative Elemental Analyses  
of Selected Polythiazyl Bromides<sup>a</sup>

	<u>%S</u>	<u>%N</u>	<u>%Br</u>	<u>Total</u>
Calc. for (SNBr) <sub>0.40</sub> <sup>b</sup>	41.09	17.95	40.96	100.00
Found	40.92	17.93	41.01	99.86
Calc. for (SNBr) <sub>0.38</sub> <sup>b</sup>	41.95	18.32	39.73	100.00
Found	42.10	18.15	39.85	100.10
Calc. for (SNBr) <sub>0.25</sub> <sup>c</sup>	48.54	21.21	30.25	100.00
Found <sup>e</sup>	48.34	21.06	30.25	99.65
Found <sup>f</sup>	48.36	21.42	30.10	99.88

<sup>a</sup> Analyses performed by Galbraith Laboratories, Inc., Knoxville, Tennessee 37921.

<sup>b</sup> Shiny, black crystalline form of (SNBr)<sub>y</sub><sup>b</sup>.

<sup>c</sup> Copper-colored crystalline form of (SNBr)<sub>y</sub><sup>c</sup>.

<sup>e</sup> From (SN)<sub>x</sub> and bromine.

<sup>f</sup> From S<sub>4</sub>N<sub>4</sub> and bromine.



Figure Captions:

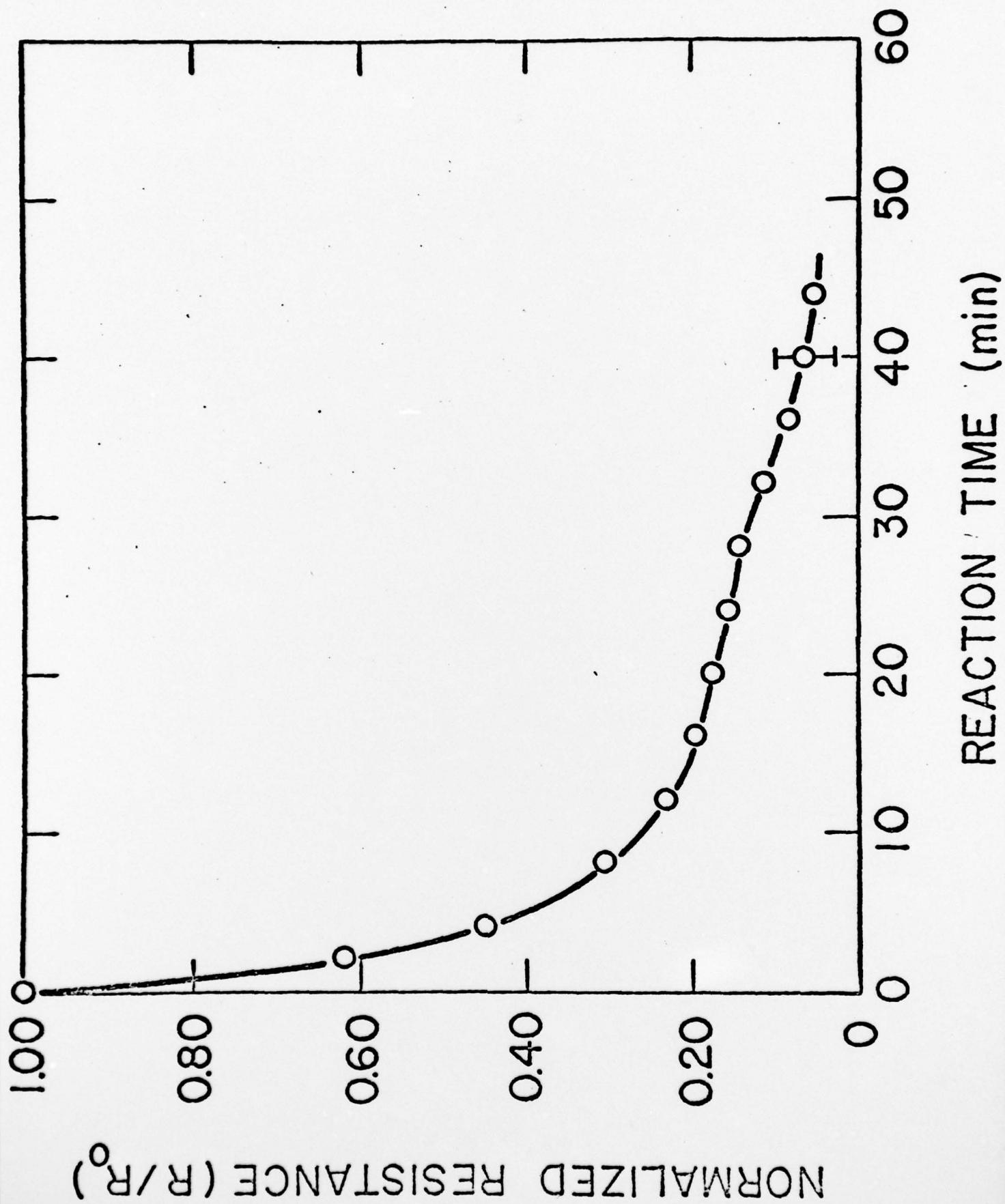
Figure 1. Normalized resistance of  $(\text{SNBr}_y)_x$  during bromination; bromine vapor pressure of 20-25 torr. <sup>y</sup>Chemical analysis of the product indicated  $y = 0.4$ ; see text. The sample conductivity was  $1.6 \times 10^3 (\Omega\text{-cm})^{-1}$  before reaction increasing to  $2.2 \times 10^4 (\Omega\text{-cm})^{-1}$  after reaction. Average value for  $\text{SNBr}_{0.4}$ ;  $\sigma(300 \text{ K}) = 3.8 \times 10^4 (\Omega\text{-cm})^{-1}$  (see text).

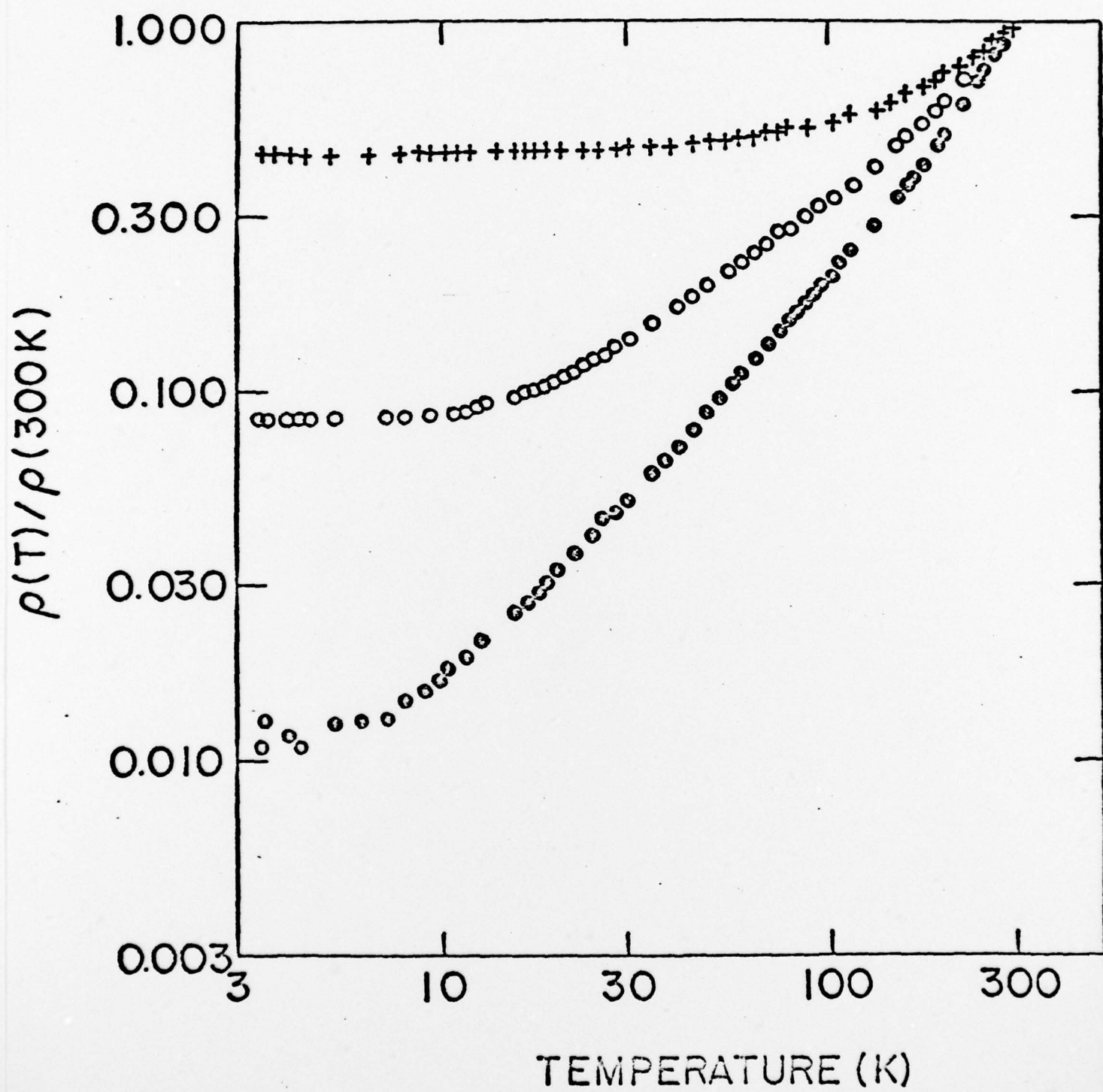
Figure 2. Temperature dependence of the resistivity of polythiazyl bromides;

●●●  $(\text{SNBr}_{0.4})_x$   
 ○○○  $(\text{SNBr}_{0.4})_x$   
 +++  $(\text{SNBr}_{0.25})_x$

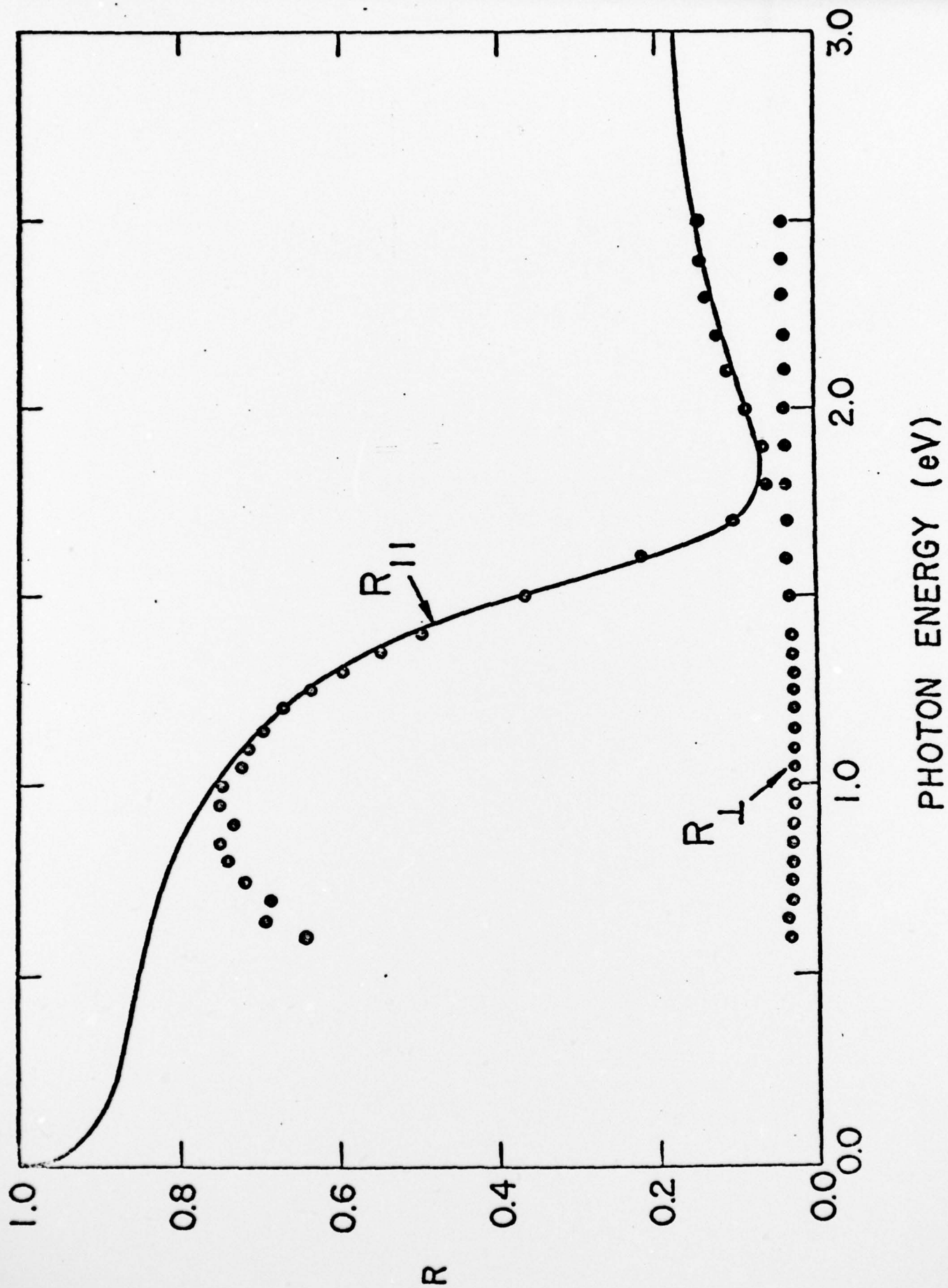
Figure 3. Polarized reflectance of  $(\text{SNBr}_{0.4})_x$  in the spectral range 0.6 eV to 2.5 eV. The solid curve represents a least-square fit arbitrarily restricting the input data to the range above 1.1 eV. The data are plotted using the absolute normalization as determined from the Drude fits.

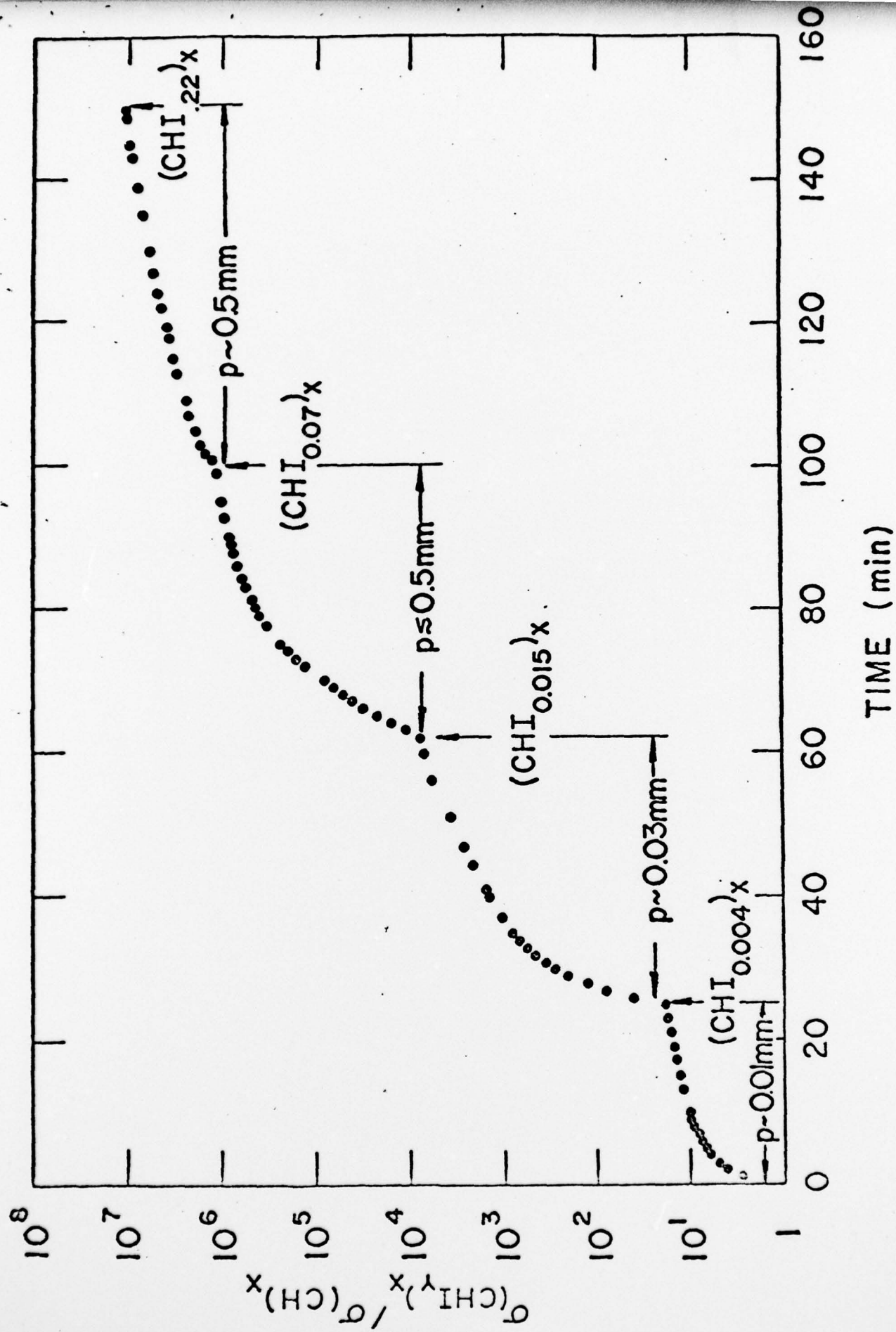
Figure 4. Increase in the room temperature conductivity of trans-polyacetylene,  $(\text{CH})_x$ , as a function of time at fixed iodine vapor pressures. The initial room temperature conductivity is  $3.2 \times 10^{-6} (\Omega\text{-cm})^{-1}$ . [In the last experiment some iodine was sublimed onto the glass walls of the conductivity apparatus in order to promote attainment of the equilibrium vapor pressure of the iodine at room temperature in the vicinity of the film.]











# TECHNICAL REPORT DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Office of Naval Research Arlington, Virginia 22217 Attn: Code 102IP	6	U.S. Army Research Office P.O. Box 12211 Research Triangle Park, North Carolina 27709 Attn: CRD-AA-IP	
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1	Commander Naval Undersea Research & Development Center San Diego, California 92132 Attn: Technical Library, Code 133	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W. S. Haynes	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Library, Code 2029 (ONRL) Technical Info. Div. Code 6100, 6170	6 1 1	Prof. Lydia M. Fenzel University of New Orleans Department of Chemistry New Orleans, Louisiana 70122	
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1		
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1		



TECHNICAL REPORT DISTRIBUTION LIST

<u>No. Copies</u>		<u>No. Copies</u>
	Dr. T. C. Williams Union Carbide Corp. Chemicals & Plastics Tarrytown Technical Center Tarrytown, New York 10591	1
	Dr. K. A. Reynard Horizons Inc. 23800 Mercantile Road Cleveland, Ohio 44122	1
	Dr. R. Soulen, Director Contract Research Department Pennwalt Corp. 900 First Avenue King of Prussia, Pennsylvania 19406	1
	<del>Dr. A. G. MacDiarmid University of Pennsylvania Department of Chemistry Philadelphia, Pennsylvania 19174</del>	1
	Dr. E. Hedaya Union Carbide Corp. Corporate Research Laboratory Tarrytown, Technical Center Tarrytown, New York 10591	1
	Dr. A. Rheingold SUNY Plattsburg Department of Chemistry Plattsburg, New York 12901	1
	Dr. C. Pittman University of Alabama Department of Chemistry University, Alabama 35486	1
	Dr. H. Allcock Pennsylvania State University University Park, Pennsylvania 16802	1
	Dr. M. Kenney Case-Western University Department of Chemistry Cleveland, Ohio 44106	
	Dr. R. Lenz Department of Chemistry University of Massachusetts Amherst, Massachusetts 01002	1
	Dr. M. Good Department of Chemistry University of New Orleans Lakefront New Orleans, Louisiana 70122	1
	Douglas Aircraft Co. 3855 Lakewood Boulevard Long Beach, California 90846 Attn: Technical Library CL 290/36-84 AUTO-Sutton	1
	NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attn: Dr. T. T. Serafini, MS 49-1	
	Dr. J. Griffith Naval Research Laboratory Chemistry Section, Code 6120 Washington, D.C. 20375	1
	Dr. G. Goodman Globe-Union Inc. 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
	Dr. E. Fischer, Code 2853 Naval Ship Research and Development Center Annapolis Division Annapolis, Maryland 21402	
	Dr. Martin E. Kaufman, Head Materials Research Branch (Code 4542) Naval Weapons Center China Lake, California 93555	